§12. Molecular Dynamics Simulation of the Structural Formation of Short Polymer Chains

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Computer simulation of the structural formation of polymer chains has recently become the focus of attention in physics, chemistry and material science. We aim at understanding the mechanisms of the structural formation of polymer chains at the molecular level. To this end, we carry out the molecular dynamics simulations of 100 short polymer chains, each of which consists of 20 CH_2 groups, and analyze the formation process of the orientationally ordered structure.

The united CH_2 groups interact via the bonded potentials (bond-stretching, bond-bending and torsional potentials) and the non-bonded potential (12-6 Lennard-Jones potential). The atomic force field used here is the DREIDING potential[1]. We use the velocity version of the Verlet algorithm and apply the Nosé-Hoover method in order to keep the temperature of the system constant. The integration time step and the relaxation constant for the heat bath variable are 0.001 ps and 0.1 ps, respectively. The cutoff distance for the Lennard-Jones potential is 10.5 Å. The polymer chains are exposed to vacuum. The total momentum and the total angular momentum are taken to be zero in order to cancel overall translation and rotation of chains. At first, we prepare random configuration of short polymer chains at high temperature (T = 700 K) and then it is quenched to various low temperatures (T = 300, 320, ..., 460 K)[2].

We show, in Fig. 1, the chain configurations at various times (t = 1, 180, 230 and 2000 ps) obtained by our MD simulations at T = 400 K. From this figure, we find the following features: (i) In the early time [Fig. 1 (a)], the configuration of polymer chains is *random*. (ii) With the elapse of time, the local orientationally-ordered regions grow in several positions [Figs. 1 (b) and (c)]. (iii) At last they coalesce into a large cluster and a highly ordered monolayer structure is formed [Fig. 1 (d)].

In order to investigate the growth process of the global bond-orientational order, we calculate the global bond-orientational order parameter S, which is defined by

$$S = \frac{1}{N(n-2)} \sum_{m=1}^{N} \sum_{i=3}^{n} \frac{3\cos^2 \psi_i^m - 1}{2}, \qquad (1)$$

where N and n are respectively the number of polymer chains and the number of CH_2 groups per polymer chain (N = 100, n = 20) and ψ_i^m is the angle between the sub-bond vector of the m-th chain $\mathbf{b}_i^m$, which is formed by connecting centers of two adjacent bonds i and $i-1$ of the m-th chain, and the director (c-axis) of the layer. The parameter S would take a value of 1.0, 0.0 or −0.5, respectively, for polymer chains whose sub-bonds are perfectly parallel, random or perpendicular to the director. We show the time dependence of S at T = 440 K in Fig. 2. This figure tells us that there are two sharp increases in the parameter S at $t \approx 150$ ps and $t \approx 240$ ps. This *stepwise* behavior is found in all our simulation results for various temperatures.

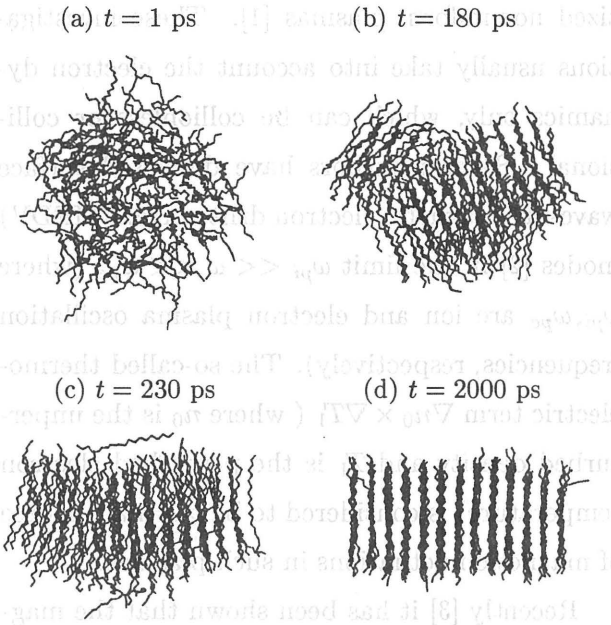

Fig. 1. The chain configurations of 100 short polymer chains for T = 400 K at various times.

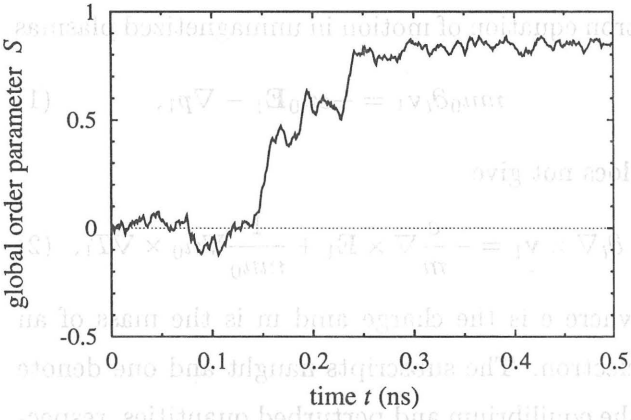

Fig. 2. The global bond-orientational order parameter S versus time t at T = 440 K.

References

1) Mayo, S.L., Olafson, B.D. and Goddard III, W.A., J. Phys. Chem. **94**, (1990) 8897.
2) Fujiwara, S. and Sato, T., Phys. Rev. Lett. **80**, (1998) 991.